

UDC 677.047.62:666.189.212

A-174 AND GVS-9 COUPLING AGENTS IN SOLUTIONS, FILMS, AND FIBERGLASS

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Translated from *Steklo i Keramika*, No. 12, pp. 9–12, December, 1999.

Transformations of A-174 and GVS-9 silanes are studied using the method of IR spectroscopy of their aqueous solutions and films depending on hydrolysis duration and aging of aqueous solutions, as well as temperature of heat treatment of films. The adhesive characteristics are investigated in fiberglass systems modified by a coupling agent and polyester resin. The optimum parameters for modification using A-174 and GVS-9 coupling agents are stated.

The transition from a planned to a market economy brought a significant modification of the range of fiberglass materials and extended the production of nonwoven fiberglass materials to reinforce polyester resin. The high strength of fiberglass is implemented in the case of a correct matching of its components. The key role of the binding component at the polymer matrix – reinforcing material interface is played by silane coupling agents. Vinyl and metacryl-containing silanes are used as modifiers for polyester binders.

The industry uses the following brands of coupling agents: vinyl triethoxysilane $\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$ GVS-9 (Russia); biocondensate Penta-61 $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCOCH}_2\text{CH}(\text{OH})\text{CH}_2)_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ (Russia), and γ -metacryloxypropyl trimethoxysilane $\text{CH}_2=\text{C}(\text{CH}_3)\text{OCO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ A-174 (Witco company, USA). Since the highest strength parameters can be achieved using the A-174 coupling agent (Table 1), this is the silane we used in production of corrosion-resistant and translucent fiberglass. The biocondensate and the GVS-9 coupling agent were used for premixes and prepregs. A significant decrease in cost when replacing A-174 coupling agent with GVS-9 coupling agent makes it preferable to use vinylsilane in the production of a wide range of polyester fiberglasses.

It was expedient to investigate the behavior of aqueous solutions of these silanes and their films using contemporary physicochemical methods with the aim of issuing practical recommendations for optimum use of the properties of these organofunctional organosilicon compounds.

The IR spectroscopy (transmission) method proved to be effective for a comparative study of organosilicon coupling agents A-174 and GVS-9. The IR spectra of water solutions

of the coupling agents were registered using an instrument used in the incomplete internal reflection method (IIRM). The structural transformations of the coupling-agent surface were evaluated using silane film IR absorption spectra on a germanium substrate.

In the IR transmission spectrum of the A-174 coupling agent, the valent asymmetric vibrations of $\text{Si}-\text{O}-\text{CH}_3$ groups correspond to the intense absorption band in the region of 1080 cm^{-1} , and the extraplanar deformational vibrations of the C-H bond in the vinyl group are reflected by the medium intensity band at 940 cm^{-1} . The absorption bands at 1160 , 1180 , 1295 , and 1320 cm^{-1} are related to the vibrations of the complex ester group $-\text{C}\equiv\text{O}$ in the coupling agent.

Figure 1 shows the IIRM spectra of A-174 coupling-agent aqueous solutions measured 2 and 24 h after preparing the solution. A comparison of the A-174 spectra in aqueous and non-aqueous solutions reveals their considerable difference, caused primarily by the reaction of hydrolysis in the coupling-agent methoxyl groups.

The intense band in the region of 1080 cm^{-1} related to the valent vibrations of the $\text{Si}-\text{O}-\text{CH}_3$ bond disappears, and another band arises at 910 cm^{-1} , determined by the valent vibrations of the $\text{Si}-\text{OH}$ group. These modifications in the spectrum indicate that 2 h after dissolution, the A-174 molecules primarily exist in the form of monomeric silane triol.

The IIRM spectrum of the solution recorded after 24-h holding exhibits a certain decrease in the intensity of the absorption band of the $\text{Si}-\text{OH}$ silanol group, and a rather intense band arises in the region of 1100 cm^{-1} with the shoulder at 1040 cm^{-1} related to the vibrations of $\text{Si}-\text{O}-\text{Si}$ siloxane groups in oligomers emerging as a consequence of

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Fig. 1. IR spectra of IIRM of A-174 coupling-agent aqueous solutions with a weight content of 1.0% and holding of 2 h (1), 1.0% and 24 h (2), and 1.5% and 24 h (3).

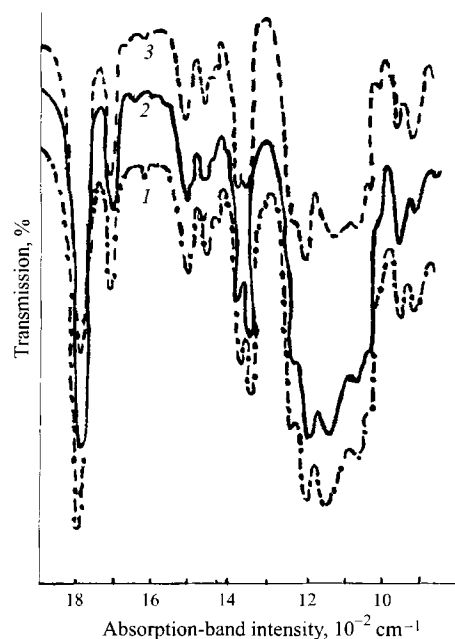


Fig. 2. IR absorption spectra of A-174 coupling-agent aqueous solutions with a weight content of 0.5% (1), 1.0% (2), and 1.5% (3).

the condensation reaction in silanol groups. As the content of the coupling-agent aqueous solution increases from 0.5 to 1.5%, the oligomerization reaction rate grows, which is indicated by the respective decrease in the relative density of absorption bands at 910 and 1100 cm^{-1} .

Figure 2 shows IR absorption spectra of the films of the A-174 coupling agent obtained from the solutions held for 2 h. A comparison of the aqueous solution spectra (Fig. 1) and the film spectra reveals their significant difference. The film spectra exhibit a substantial decrease in the intensity of the valent vibrations band of SiOH silanol groups in the region of 910 cm^{-1} and increased intensity of absorption bands of siloxane groups in the range 1120 – 1000 cm^{-1} .

It should be noted that the most structurally sensitive area in organosilicon compounds is the area of asymmetric valent vibrations of the Si – O – Si bond. The presence of two intense bands in the region 1120 – 1100 and 1045 – 1030 cm^{-1} points to a high degree of oligomerization in the A-174 films compared to the solution. However, the coupling-agent film also contains a certain amount of Si – OH group, although significantly lower than the solution does.

The internal structure of the proper oligomeric siloxane which forms the film of the A-174 coupling agent is of special interest. It is similar to the structure of oligomeric methylsilsequioxane [1] and contains large (1115 cm^{-1}) and small (1040 cm^{-1}) cycles. The latter arise in reactions of

TABLE 1

Coupling agent	Weight content, %	Fixation temperature, °C	Bending strength of model polyester fiberglass, MPa			
			initial	after boiling in water*	after holding in alkali*	after holding in acid*
Silquest, A-174 (Witco, USA)	0.5	100	863	708	784	666
	0.5	150	793	711	631	556
	0.5	200	872	774	801	724
	1.0	100	845	621	672	648
Bicondensate Penta-61 (Russia)	0.5	100	791	702	697	664
	0.5	150	702	693	615	660
	0.5	200	708	544	589	500
	1.0	100	780	640	683	613
Organosilicon liquid GVS-9 (Russia)	0.5	100	692	560	440	448
	1.0	100	739	628	485	472
	1.0	150	718	620	467	460
	1.0	200	648	342	258	232

* For 72 h.

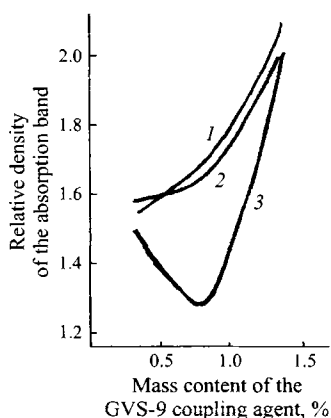


Fig. 3. Relationship of the relative content of Si – OH groups in GVS-9 coupling-agent film and the concentration of initial aqueous solution with a holding duration of 2 h (1), 24 h (2), and 48 h (3).

condensation of oligomeric chains (interchain condensation) and internal cyclization, respectively.

It is known that the increased concentration of the solution facilitate the priority of the internal cyclization reaction [2]. This regularity is observed also in the case of the A-174 organosilicon coupling agent.

The studies of IR spectra of films produced after holding A-174 solutions in the interval from 2 to 72 h revealed that they are virtually identical. Apparently, the condensation reactions taking place in the drying film, as the solution concentration increases, level all differences in the oligomer structure existing in the solutions.

The effect of heat treatment on the structure of films made of 0.5% solution of A-174 coupling agent was investigated. The films were held at 100, 150, and 200°C for 15 min. The increased intensity of the absorption band of siloxane groups in the region of 1115 cm^{-1} with a constant intensity of the band at 1040 cm^{-1} points to the fact that heat treatment at temperatures of 100 – 150°C results in further condensation of oligomeric chains, whereas the interchain condensation prevails.

An increase in the treatment temperature from 150 to 200°C significantly decreases the number of double bonds (the ratio of the optical density of the valent-vibrations band of the C = C bond in the region of 1630 cm^{-1} to the band of

the C = O bond in the polyester group of the coupling agent at 1720 cm^{-1}).

The IIRM spectrum of aqueous solution of GVS-9 organosilicon coupling agent exhibits a band in the region of 900 cm^{-1} determined by the valent vibrations of the Si – OH group, which indicates the reaction of hydrolysis in the ethoxy groups.

The film spectra of A-174 and GVS-9 coupling agents coincide in the existence and position of the absorption bands of siloxane Si – O – Si and silanol Si – OH groups. At the same time, there are certain differences in the IR spectra of the oligomer films considered. Thus, the intensity of the band at 900 cm^{-1} and, accordingly, the amount of residual silanol groups is higher in the GVS-9 film than in the A-174 film. This can be accounted for by the more intense condensation reaction in the A-174 solutions. Moreover, the ratio of the vibration-band intensity of Si – O – Si groups in the regions of 1040 and 1115 cm^{-1} characterizing the internal structure of siloxane films points to a higher content of short cycles and a lower degree of interchain condensation in the GVS-9 coupling-agent structure compared to the A-174 coupling agent.

The content of silanol groups in GVS-9 films based on solutions of varying concentration and varying duration of holding after preparation is shown in Fig. 3. The quantity of silanol groups was estimated from the intensity of the Si – OH band at 900 cm^{-1} normed by the absorption intensity of the vinyl group – CH = CH₂ at 970 cm^{-1} . The resulting dependences can probably be interpreted in the following way. In holding the aqueous solution of GVS-9 coupling agent up to 24 h, the increase in hydrolysis rate exceeds the condensation rate for a coupling-agent content equal to 0.5 – 1.5%. As the hydrolysis duration increases to 48 h, the complex character of the dependence of the silanol-group content in the solution on the solution concentration becomes evident, which is similar to the dependence earlier established for the A-174 coupling agent.

The heat-treatment conditions have a significantly greater effect on the structure of GVS-9 film than in the case of the A-174 coupling agent.

The intensity of the absorption band at 1040 cm^{-1} in the IR spectra of GVS-9 films after heat treatment at 100 – 200°C increases, and the intensity of the absorption band at 1115 cm^{-1} virtually does not change (the variations in the IR spectra of the A-174 coupling agent are the reverse). This shows that the prevailing direction of subsequent condensation of oligomeric siloxanes based on GVS-9 solutions is interchain and not intramolecular cyclization. It can be assumed that the resulting polymer will have a looser, less spatially tied structure than the polymer based on the A-174 coupling agent.

As for the heat-treatment effect on the concentration of vinyl groups – CH = CH₂, it is significantly lower than in the case of the methacrylic group in the A-174 coupling agent. The intensity of vibration bands of the vinyl group (1605, 1020 cm^{-1}) in the IR spectra of GVS-9 films heat treated at

TABLE 2

Coupling agent*	Adhesive strength, MPa			
	initial	after the effect of		
		boiling H ₂ O	10% KOH	25% H ₂ SO ₄
A-174	18.9	11.3	6.1	9.2
GVS-9	15.1	8.4	5.5	4.8

* Weight content of coupling agent 0.5%; the temperature of its fixation 100°C; exposure 5 min.

200°C changes insignificantly. This is probably due to the lower reactivity of the vinyl group in the GVS-9 coupling agent as compared to the methacrylic group in the A-174 coupling agent.

Adhesion in the system "fiber glass modified with a coupling agent – PN-15 polyester resin" was studied for the specified coupling agents with the aim of optimizing their use. The data on adhesive strength and the effect of aggressive media on it are given in Table 2 (hydrolysis duration 2 h).

The influence of the reacting capacity of the double bonds of coupling agents on the efficiency of interaction with the polyester matrix is manifested in the different adhesive strength shown in the initial state and substantial differences after the action of aggressive media.

Experimental data on the effect of a number of factors (concentration, hydrolysis duration, temperature of coupling-agent fixation) on the strength of the interface bond prove that the optimum content of the A-174 coupling agent is 0.5% (Table 3). This agrees well with the data of IR spectroscopy indicating that with increasing concentration of A-174 solution, the direction of oligomerization reactions is changed, and surface structures emerge which are only slightly effective in the formation of an adhesive bond.

The duration of A-174 holding does not have a perceptible effect on adhesive strength. This is due to the fact that hydrolysis is virtually completed in 2 h, and further transformations ensure the efficiency of the coupling agent over several days.

The optimum fixation temperature of the A-174 coupling agent is 100 – 125°C, which agrees with the data of IR spectroscopy indicating a substantial decrease in the quantity of double bonds in the coupling-agent film with increasing temperature.

In the case of GVS-9 silane (Table 3), the optimum duration of the aqueous-solution holding is 24 h. According to the IR spectroscopy data, that time is required for a sufficiently complete hydrolysis reaction and corresponds to the initial stage of the condensation reaction. It is established that their maximum adhesive strength is accomplished with a coupling agent content of 0.75 – 1.25%.

The optimum temperature of GVS-9 coupling-agent fixation on glass fiber is 125°C. This agrees with the data obtained in studying the stability of the GVS-9 vinyl group in the heat-treated coupling-agent film. With increasing temperature, the intensity of the vinyl group – $\text{CH}=\text{CH}_2$ decreases, apparently due to the polymerization reaction. The latter decreases the quantity of the coupling-agent groups active with

TABLE 3

Coupling agent	Weight content, %	Fixation temperature, °C	Adhesive strength in the system fiberglass – polyester resin, Mpa in hydrolysis duration, h		
			2	24	48
A-174	0.25	100	17.2	17.0	16.9
	0.25	125	17.0	16.8	16.9
	0.25	150	15.1	15.0	14.7
	0.50	100	18.9	19.3	18.8
	0.50	125	18.7	18.7	18.5
	0.50	150	16.3	14.8	15.7
	1.00	100	16.2	15.6	15.8
	1.00	125	16.4	16.0	16.2
	1.00	150	14.7	12.9	14.4
	1.25	150	13.4	13.6	13.0
GVS-9	0.25	100	14.7	14.8	14.3
	0.25	125	15.0	15.1	14.7
	0.25	175	14.8	14.5	12.8
	0.75	75	11.4	12.5	12.0
	0.75	100	16.8	17.3	16.0
	0.75	125	17.2	18.1	16.8
	0.75	175	12.7	10.0	11.9
	1.25	75	16.4	16.9	13.7
	1.25	100	21.7	23.5	19.8
	1.25	125	22.3	24.6	20.1
	1.25	175	20.3	19.8	18.5

respect to the resin and is manifested in decreased adhesive strength.

Thus, the application of the IR spectroscopy method to aqueous solutions of industrially used silanes makes it possible to control the process of acid-catalyzed hydrolysis of coupling agents.

The potential of the considered coupling agents in glass fibers is realized if silane trianols and macromolecular structures arising as a consequence of interchain condensation reactions prevail on the glass fiber surface in aqueous solutions and films.

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